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CERAMIC EUTECTICS

FREDERICK SCHMID and DENNIS J. VIECHNICKI
CERAMICS DIVISION

March 1972

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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Technical Report by

FREDERICK SCHMID AND DENNIS J. VIECHNICKI

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13. ABSTRACT

Metal oxide ingots with fine grain size can be fabricated by growth from the melt. An oriented lamellar-type microstructure free of cracks is developed in the Al_2O_3/ZrO_2 eutectic system by controlled solidification with the gradient furnace. The colonies inherent in ingots grown by a modified Bridgman technique have been eliminated and also a lamellar-type rather than a rod-type microstructure is produced in ingots grown with the gradient furnace.

Cracking does not occur at the eutectic grain boundaries as it does for polycrystalline aggregates of Al_2O_3, $MgAl_2O_4$, or $Y_3Al_5O_{12}$ solidified from the melt. (Authors)

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INTRODUCTION

Ceramic eutectic systems have potential for structural applications at high temperatures since they may not be as susceptible to thermal shock as single component systems. Ingots fabricated by solidification from the melt have fine eutectic microstructures. The large boundary area inherent in fine grain eutectics may deflect cracks; this is especially true if there is a large mismatch of the crystallographic planes at the eutectic phase boundaries. Structures produced from the melt are also very stable since the phases are well reacted. From a processing point of view, eutectics are relatively easy to fabricate since their melting point is lower than the terminal components.

By controlling the solidification parameters, growth rate and temperature gradient, and impurities, either random or oriented eutectic microstructures can be produced. The random structures would probably result in isotropic properties and the oriented structures would produce anisotropic properties.

The study was undertaken to investigate the high melting point eutectic system Al_2O_3/ZrO_2 to determine whether: (1) sound, crack-free ingots could be solidified; (2) homogeneous eutectic structures free of colonies and banding could be produced; and (3) oriented rod-type or lamellar-type eutectic structures could be solidified in large ingots.

Viechnicki and Schmid[1] have studied eutectic solidification in the $Al_2O_3/Y_3Al_5O_{12}$ system. The system Al_2O_3/ZrO_2 was chosen for this study since this is a simple high-temperature binary system with no compound formation,[2] both Al_2O_3 and ZrO_2 have low vapor pressure below 2000 C and they are not easily reduced to suboxides or metals. The eutectic point was reestablished at 63 mol % Al_2O_3, 37 mol % ZrO_2 and 1870 ± 5 C.[3] The volume fraction, volume ZrO_2/volume Al_2O_3, was found to be 0.506 at the eutectic.[3] The Al_2O_3 is the first phase to nucleate when eutectic growth occurs.[3]

EXPERIMENTAL

Materials

The purities of the starting alumina* and zirconia† powder used in this investigation were greater than 99.99% and 99.0%, respectively. The powders (corrected for moisture absorption) were weighed in the desired proportions and mixed in a ball mill for 12 hours in acetone, dried and calcined for more than 72 hours at 1200 C. The calcined powders were either put directly into crucibles

*Gem — 242 Ultra High Purity Alumina Engineering Materials, P.O. Box 363, New York 8, New York. Typical impurities listed by the producer were 0.003% Na_2O, 0.001% SiO_2, 0.001% TiO_2, 0.001% Fe_2O_3, 0.001% P_2O_5, and 0.001% Cl.

†Zircoa A-H-C-, Zirconium Corporation of America, 31501 Solon Rd, Solon 39, Ohio. The zirconia powder contained greater than 99% ZrO_2 plus HfO_2. Maximum specific impurities listed by the producer include 0.18% SiO_2, 0.22% CaO, 0.15% MgO, 0.10% Fe_2O_3, 0.16% Al_2O_3, and 0.11% TiO_2.

for Bridgman solidification or cold pressed and sintered at 1600 C 1 hour in vacuum and put in a crucible for gradient furnace solidification.

Unidirectional Solidification Bridgman Method

Calcined powders were packed into vapor-deposited tungsten crucibles* 1.3 cm in diameter and 30 cm long. After initial melting at 1900 C the 20 grams of loose-packed powder resulted in a 10-cm-long ingot.

The bottom was cut off the crucible to eliminate a reflective interface and increase radiation cooling. Melting and unidirectional solidification was conducted in the modified Bridgman type furnace illustrated in Figure 1. One atmosphere of helium was utilized for all solidification studies. The power was supplied by a 450 kHz 20 kW rf generator to a graphite susceptor 2.5 cm in diameter and 15 cm long. The melts were stabilized at 2000 C. The bottomless crucibles were positioned so they extended 1.3 cm below the bottom of the susceptor. Unidirectional solidification was accomplished by lowering the crucible through the zone at the desired rate. Temperatures were measured on the bottom of the ingot with an optical pyrometer. These temperatures were corrected for losses.[4]

Temperature gradients in the solid were determined by measuring the distance between the bottom of the ingot and the position of the lowest interface. This was measured on the sectioned ingot. The difference between the melting temperature at the lowest interface and the corrected bottom temperature was divided by this distance to obtain the temperature gradient in the solid at the start of solidification.

Unidirectional Solidification Gradient Furnace Method

Sintered discs of the Al_2O_3/ZrO_2 weighing approximately 250 grams were placed in a shear-spun molybdenum crucible† 5 cm in diameter and 5 cm high. The crucible was seated on the heat exchanger of the gradient furnace as illustrated in Figure 2. The tungsten heat exchanger extends into the heat zone of a graphite vacuum resistance furnace.‡ The temperature of the heat zone was measured with an optical pyrometer and the heat exchanger temperature was measured with a W-W/26Re thermocouple.

The melt was superheated 100 C above the melt temperature in a 5×10^{-2} torr vacuum. After the furnace was stabilized at 1970 C the helium flow was gradually increased until the desired heat exchanger temperature was attained. Solidification was controlled by decreasing the furnace power at the desired rates. The position of the growth interface before and after unidirectional solidification could be determined on the sectioned ingot. This distance divided by the time to decrease the temperature below the melting point is the approximate growth rate. The approximate temperature gradients were determined by

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*San Fernando Laboratories, 10258 Norris St., Pacoima, California.

†Fansteel Metallurgical Corp., Metals and Fabrication Division, North Chicago, Illinois

‡Astro Industries Inc., 1330 Cacique St., Santa Barbara, California.

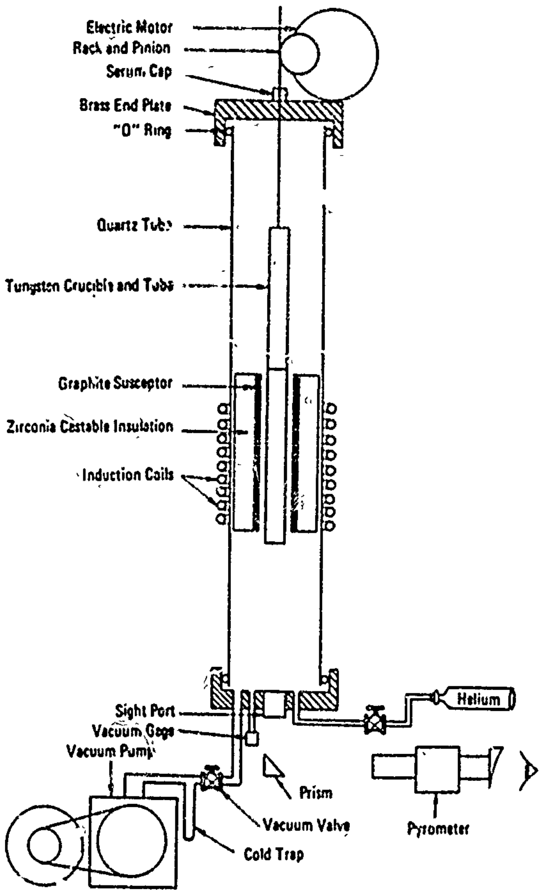

Figure 1. Schematic of Bridgman type furnace.
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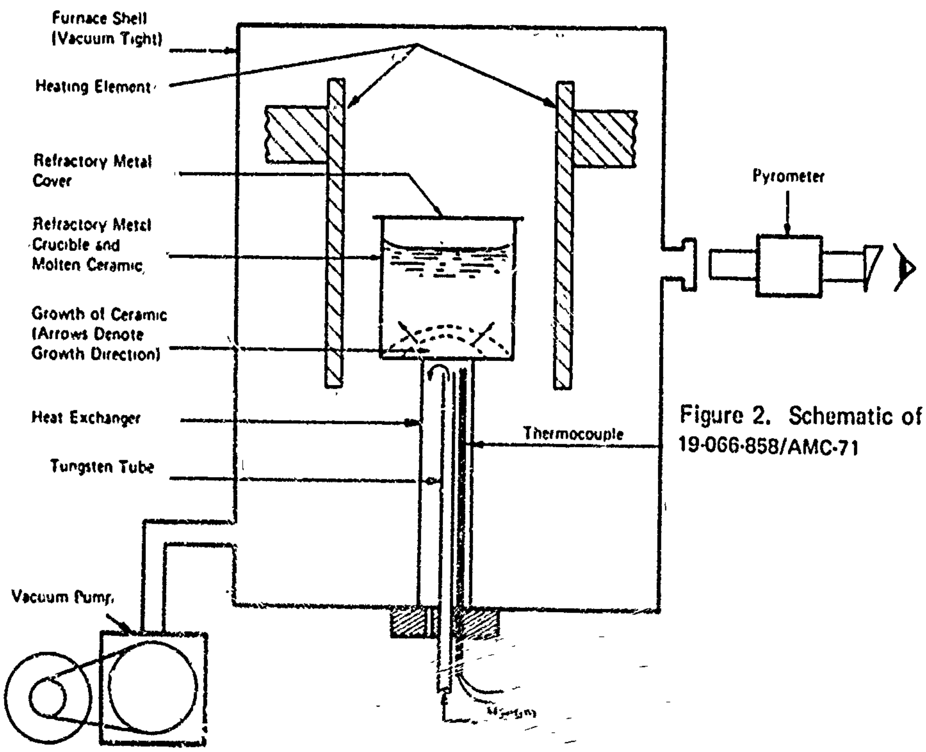

Figure 2. Schematic of gradient furnace.
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measuring the positions of the interfaces at the start and finish of solidification from a polished section, and dividing this distance into the difference between the eutectic temperature and the temperature at the bottom of the crucible at the start of solidification.

Optical and X-Ray Examination

After solidification the ingots were cut in half and transverse sections of various areas were cut. Polished end sections were prepared from these samples by using graded silicon carbide papers, diamond paste, and chromic oxide for a final relief polish. A Bausch and Lomb metallograph with a carbon arc light source was used to make photomicrographs. Phase analysis of the solidified ingots was conducted with a Norelco Diffractometer utilizing CuKα X radiation.

RESULTS AND DISCUSSION

Unidirectional Solidification by the Bridgman Method

Ingots were solidified at growth rates ranging from 1.29 cm/hour to 15.56 cm/hour. All ingots consisted of columnar grains approximately 0.1 mm in diameter and 4 mm long. The ingots were pore-free but banding occurred in all ingots. Banding resulted from changes in growth rate or disturbance of the liquid/solid interface. Typical longitudinal and transverse microstructures are presented in Figures 3 and 4. The ingot was solidified at 2.59 cm/hour, with a 220 C/cm temperature gradient at the start of solidification. Colonies are evident in both photomicrographs. They appear as cells in the transverse sections, Figure 4, and bands parallel to the growth direction in the longitudinal section, Figure 3. Within the colonies are fine, highly oriented rod-type eutectic microstructures with very straight rods 1 μm in diameter and more than 50 μm in length. Figure 5 shows a transverse section and Figure 6 a longitudinal section. Near the colony boundaries the microstructure becomes less oriented as is evident in Figure 7, a longitudinal section near a colony boundary. Polishing of the longitudinal sections was difficult due to pullouts seen in Figures 6 and 7. This can be explained by the fact that the alumina matrix is in tension. Zirconia undergoes a tetragonal to monoclinic phase transformation between 900 and 800 C.[5] The ZrO_2 expands during this transformation and puts the Al_2O_3 matrix in tension below 800 C. Localized radial temperature gradients caused by the rejection of impurities at the colony boundaries probably cause the misoriented eutectic structure near the colony boundaries while near the center of the colonies the microstructure is highly oriented.

Processing problems encountered in induction heating with the rf generator were thermal asymmetry due to localized temperature gradients, vibrations due to lowering of the crucible and power fluctuations. These conditions could cause convection in the liquid and a nonplanar interface; this probably contributes to colony formation.

To overcome the thermal asymmetry, vibrations, and temperature fluctuations, a gradient furnace method developed by Schmid and Viechnicki[6] was utilized.

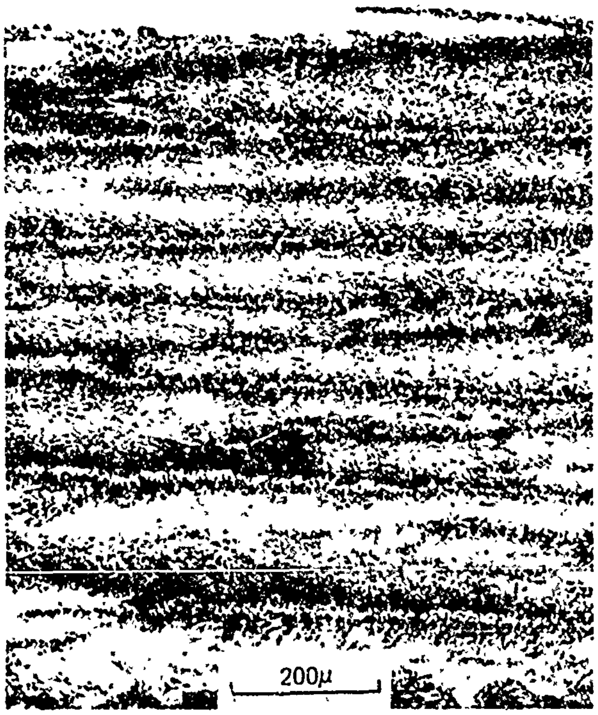

Figure 3. Longitudinal section of colony structure in an ingot of eutectic composition, 63.0 mol % Al_2O_3/37.0 mol % ZrO_2. 19-066-1257/AMC-69

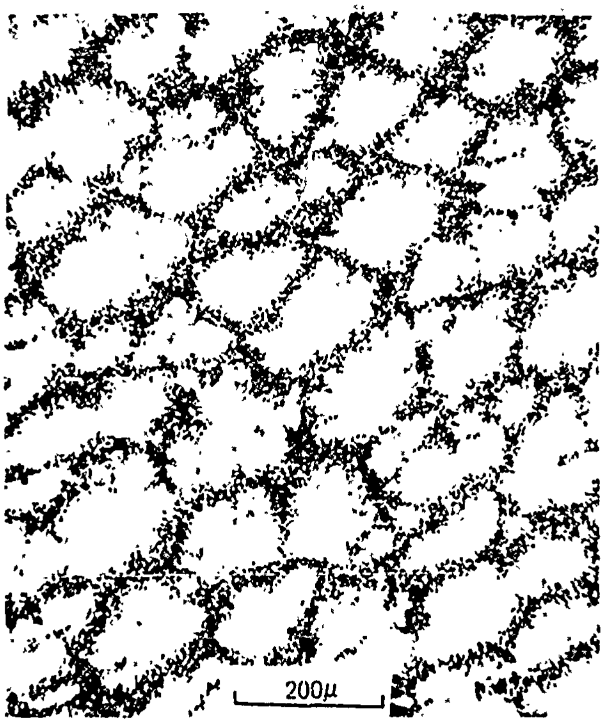

Figure 4. Transverse section of colony structure in an ingot of eutectic composition, 63.0 mol % Al_2O_3/37.0 mol % ZrO_2. 19-066-1256/AMC-69

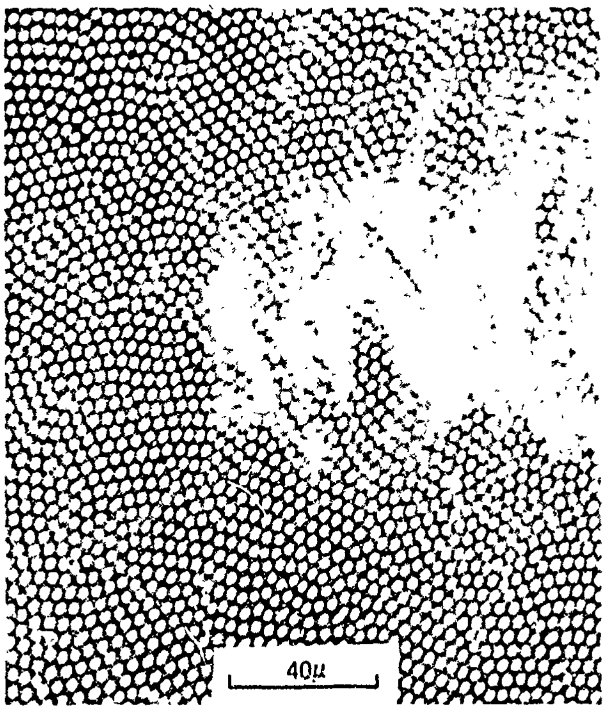

Figure 5. Transverse section of highly oriented rod-type eutectic microstructure of 63.0 mol % Al_2O_3/37.0 mol % ZrO_2 composition. 19-066-1258/AMC-69

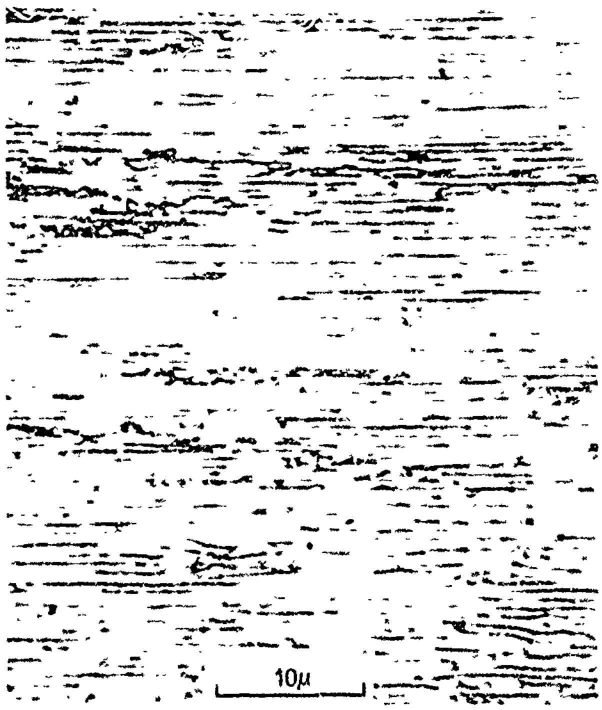

Figure 6. Longitudinal section of highly oriented rod-type eutectic microstructure of 63.0 mol % Al_2O_3/37.0 mol % ZrO_2 composition. 19-066-1254/AMC-69

Unidirectional Solidification Gradient Furnace Method

The method utilized to grow sapphire boules up to 15 cm in diameter was modified to solidify eutectics. Ingots were unidirectionally solidified at 0.75 and 1 cm/hour. Figure 8 is a longitudinal cross section of an Al_2O_3/ZrO_2 eutectic ingot, 5 cm in diameter, solidified at approximately 0.75 cm/hour with a starting temperature gradient of approximately 1200 C/cm, in the solid. The growth interface is delineated by banding.

Banding is due to changes in the growth rate. This results when the temperature is not decreased at a constant rate, i.e., manually controlled. Columnar eutectic grains can easily be seen; some grains increase in size at the expense of the less favorably growth-oriented grains. A crack is evident along one of the grains. This may result from the tensional stress that exists in the matrix. The void in the top right-hand corner is solidification shrinkage; it delineates the end of unidirectional solidification.

Typical eutectic microstructures of longitudinal and transverse cross sections from the ingot described above are presented in Figures 9 and 10. The longitudinal microstructure is similar to that solidified by the Bridgman method. However, the transverse photomicrograph shows that the microstructure is no longer rod, but a lamellar-type eutectic microstructure. Figure 11 is a photomicrograph of the same transverse section at lower magnification to show a larger area. This shows that the colony structure present in ingots solidified by the Bridgman technique has been completely eliminated. Even at the grain boundary delineated by the light and dark areas the eutectic structure is homogeneous. Colonies were completely eliminated in all the ingots solidified in the gradient furnace regardless of the solidification parameters (growth rates greater than 1 cm/hour and gradients in the solid less than 500 C/cm).

Figure 12 is the eutectic microstructure from a longitudinal section of an ingot solidified at 1 cm/hour with a 600 C/cm gradient in the solid at the start of solidification. It is interesting to note that the eutectic microstructure of one grain is highly oriented while the other is randomly oriented. This indicates the alinement of the microstructure is heavily dependent on the orientation of the grains. The pullouts that exist in the microstructures solidified by the Bridgman method are also apparent in the microstructures fabricated with the gradient furnace.

Homogeneous eutectic structures free of colonies can be fabricated by the modified gradient furnace method. The large temperature gradients that are imposed with minimum thermal asymmetry is probably a big factor in achieving this goal. Since there is no motion in this process and the thermal gradient is arranged so the coldest material is on the bottom, there is no turbulence due to convection and vibrations. This should also be beneficial to solidifying homogeneous microstructures. Another advantage of this method is the fact that the impurities are rejected out to the crucible wall. From a practical point of view, this method is very flexible, since large size and various shaped ingots can be unidirectionally solidified.